Effect of magnesium sulfate on various properties of lithium formate monohydrate crystals

G.Emerson Robin, U.Sankar, T.Chithambarathanu, P.Selvarajan

Abstract— **Undoped and magnesium sulphate doped lithium formate monohydrate crystals have been grown by slow evaporation solution growth technique. Solubility studies for the samples were carried out in the temperature range 30 to 60 oC. X-ray diffraction studies confirm that the grown crystals crystallize in orthorhombic system. Mechanical parameter such as microhardness was evaluated by Vicker's hardness test. Laser damage threshold values were measured for the samples. SHG efficiency was measured using a Nd.YAG laser. The measurement of dielectric constant, dielectric loss of the grown crystals was carried out at different frequencies. EDAX studies were made to identify the elements present in the samples. The results obtained from the various studies of the grown crystals were discussed.**

Index Terms— **Single crystal; solution growth; NLO; SHG; XRD; hardness; EDAX; dielectrics**

I. INTRODUCTION

Nonlinear optical (NLO) materials are useful in the field of telecommunications, optical computing and optical information process [1,2]. NLO materials are classified into organic, inorganic and semiorganic materials. Inorganic NLO materials possess high melting point, high mechanical strength, and high degree of chemical inertness but poor optical nonlinearity. Organic NLO materials have low melting point, low mechanical strength, high degree of delocalization due to their weak Van der Waal's and hydrogen bondings and also they have the flexibility in the methods of synthesis, scope for altering the properties by functional substitution, inherently high nonlinearity, high laser damage threshold values [3-5].

In recent years, many researchers are working on semiorganic NLO materials which are the combination of high optical nonlinearity of organic compounds with the favorable mechanical and thermal properties of inorganic materials [6-8]. Lithium formate is a semiorganic material which crystallizes in orthorhombic system and it is a non-centrosymmetric crystal [9,10]. In this work, lithium formate monohydrate crystals were grown using commercially available lithium formate monohydrate by slow evaporation method. To improve the various properties of lithium formate crystals, magnesium sulfate was added and the doped crystals were also grown by slow evaporation method. The harvested crystals were characterized by various studies and the results are discussed.

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II. METHODOLOGY

A. Crystal growth

The sample used in this work was lithium formate monohydrate which was purchased commercially. To get the magnesium sulfate doped lithium formate sample, 1 mole% of magnesium sulfate was added to lithium formate sample. The purity of the sample was improved by re-crystallization process. Saturated solutions of the undoped and magnesium sulfate doped lithium formate samples were prepared separately using double distilled water as the solvent. The prepared solutions were stirred well using a hot plate magnetic stirrer for about 2 hours and filtered using the Whatmann filter papers. Then the solutions were taken in growth vessels and due to slow evaporation process, single crystals of the samples were harvested after a period of nearly one month.

B. Characterization techniques

The grown single crystals were characterized by single crystal X-ray diffraction studies using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK$_\alpha$ (λ=0.71069 Å) radiation to evaluate the lattice parameters. To confirm the nonlinear optical property, Kurtz and Perry powder SHG test was carried out for the grown crystals using Nd:YAG Q-switched laser[11]. Microhardness analysis was carried out using Vickers microhardness tester fitted with a diamond indenter and two trials have been carried out to ascertain the correctness of the values. Vickers microhardness values have been calculated by using the formula $H_v = 1.8544\ P / d^2$ kg/mm^2 where H_v is the Vickers microhardness number, P is the applied load in kg, d is the mean diagonal length of the indentation in mm and 1.8544 is a constant for the geometrical shape of diamond pyramidal indenter.Values of dielectric constant and dielectric loss of the sample crystals were measured using LCR meter (Agilent 4284A) in the frequency region 100 Hz-1 MHz.

III. RESULTS AND DISCUSSION

A. Measurement of solubility

Solubility study was carried out using a magnetic stirrer and a constant temperature bath by gravimetrical method [12]. The grown sample was added step by step to 20 ml of double distilled water in an air-tight container kept in the CTB and the stirring was continued till a small precipitate was formed at 30 ^{o}C. Then, 5 ml of the solution was pipetted out and taken in a petri dish and it was warmed up till the solvent

was evaporated out. By measuring the amount of salt present in the petri dish, the solubility (in g/100 ml) of the sample water was determined. The same procedure was followed to find solubility of magnesium sulphate doped lithium formate sample. Variation of solubility with temperature for the samples are shown in figure 1. The results show that the solubility increases with temperature and it slightly increases when magnesium sulfate is added as the dopant. The figure 1 has three regions viz. supersaturated region above the curve, saturated region along the curve and undersaturated region below the curve and the solubility data will be useful to prepare saturated and supersaturated solutions at any temperature in the range 30-60 °C.

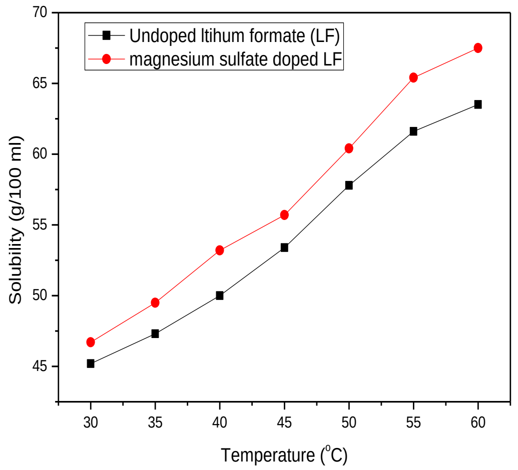

Fig.1: Variation of solubility with temperature for undoped and magnesium sulfate doped lithium formate monohydrate samples

B. Identification of crystal structure

The structure of the grown crystals was identified by using a single-crystal X-ray diffractometer (Model: ENRAF NONIUS CAD-4, MoK_α (λ = 0.71069 Å) and the lattice parameters were obtained. The obtained lattice constants for the grown undoped lithium formate crystal are a= 4.848 (2), b= 6.502(3) Å , c = 9.958(4) Å and $\alpha = \beta = \gamma = 90^o$ and those for magnesium sulfate doped lithium formate crystal are a = 4.797 (3), b= 6.516(4) Å , c = 9.964(2) Å and $\alpha = \beta = \gamma = 90^o$. The results show that the grown crystals belong to orthorhombic structure and the crystal structure has not been altered when magnesium sulfate was added into lithium formate crystals as the dopant.

C. NLO studies

NLO test can be checked by measuring the Second Harmonic Generation (SHG) efficiency and it was tested for the grown crystals of undoped and magnesium sulfate using the powder technique of Kurtz and Perry using a pulsed Nd:YAG laser(Model: YG501C, λ=1064 nm). The grown crystals were ground to powder of grain size 150-175 µm and the input laser beam was passed through IR reflector and directed on the powdered sample. Potassium Dihydrogen Phosphate (KDP) was used as the reference sample. The SHG behavior was confirmed by the emission of green light (λ = 532 nm) from the sample. The relative SHG efficiency values obtained are 1.12 and 1.35 respectively for undoped lithium formate and magnesium sulfate doped lithium formate crystals. The effect of magnesium sulfate doping into lithium formate crystal is observed to increasing the SHG efficiency.

D. Measurement of hardness

Hardness is one of the mechanical constants and this can be determined by carrying out microhardness studies. Microhardness property was measured using a Vickers microhardness tester, fitted with a Vickers diamond pyramidal indenter. The variations of hardness number with load for the grown crystals are shown in the figure 2. The result shows that the hardness increases with increase of load. It is noticed that the hardness is altered when lithium formate crystals are doped with magnesium sulfate and this may be due to the incorporation of impurities in the lattice of lithium formate crystals.

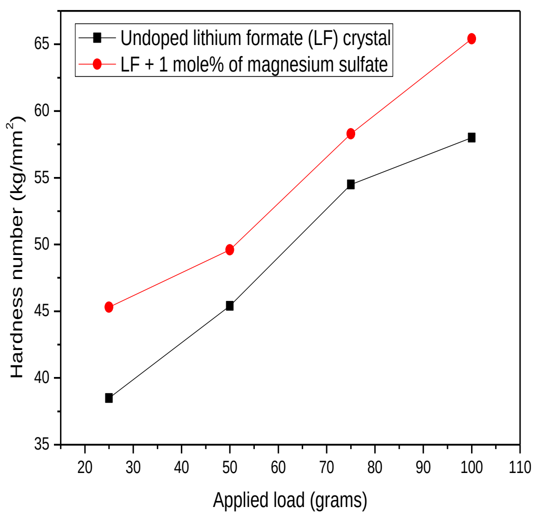

Fig.2:Variation of hardness number with applied load for undoped and magnesium sulfate doped lithium formate monohydrate crystals

E. Measurement of dielectric constant and loss factor

Dielectric parameters such as dielectric constant and loss factor for the samples were measured by parallel plate capacitance method using an LCR meter. The dielectric loss factor can be measured directly from the LCR meter. The variations of dielectric constant and dielectric loss with frequency for undoped and magnesium sulfate doped lithium formate monohydrate crystals are shown in the figures 3 and 4. It is observed that the dielectric constant has higher values at lower frequencies and further it decreases with increase in frequency and become independent at higher frequencies. The dielectric constant of the materials is due to the contribution of electronic, ionic, dipolar or orientation and a space charge polarization which is dependent upon on the frequencies. The space charge polarization is generally active at lower frequencies. It is observed that the dielectric loss decreases with the increasing of frequency. The low value of dielectric loss with high frequency for the samples suggests that the sample possess enhanced quality with lesser defects [13,14].

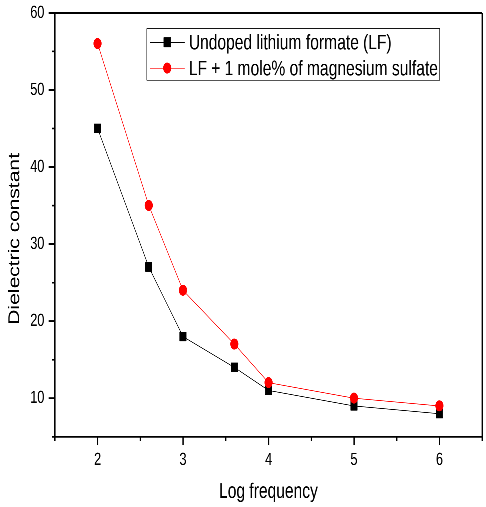

Fig.3: Variations of dielectric constant with frequency for undoped and magnesium sulfate doped lithium formate crystals

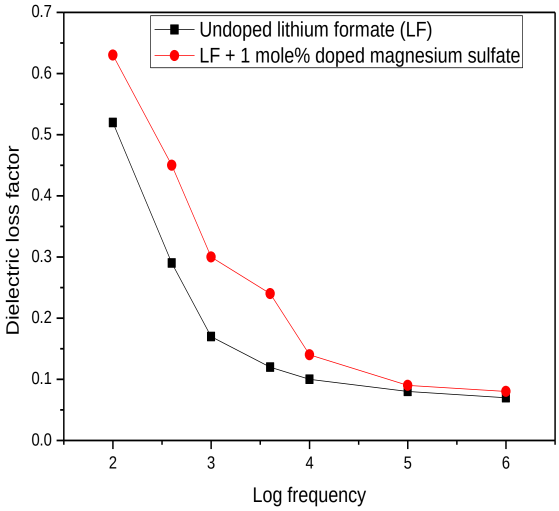

Fig.4: Variations of dielectric loss factor with frequency for undoped and magnesium sulfate doped lithium formate crystals

F. Laser damage

Laser damage threshold (LDT) values for the samples were obtained using an Nd:YAG laser (1064 nm, 18 ns pulse width). The energy of the laser beam was measured by Coherent energy/power meter (Model No. EPM 200) and LDT values were determined. The obtained value of LDT of the grown lithium formate monohydrate crystal is 1.46 GW/cm^2 and that for magnesium sulfate doped lithium formate crystal is 1.63 GW/cm^2. The higher values of LDT indicate that the samples can be used for optoelectronic devices.

G. EDAX studies

Energy Dispersive Analysis by X-rays (EDAX) technique a chemical microanalysis method used in conjunction with scanning electron microscopy (SEM). This technique detects X-rays emitted from the sample during bombardment by an electron beam to characterize the elemental composition of the sample. The data generated by EDAX analysis consists of spectra showing peaks corresponding to the elements making up the true composition of the sample being analyzed. EDAX spectra were recorded using scanning electron microscope (Vega3 Tescan model) and they are presented in the figures 5 and 6. From the results it is confirmed that the elements such as carbon, oxygen, magnesium and sulphur are present in the undoped and magnesium sulfate doped lithium formate crystalline samples.

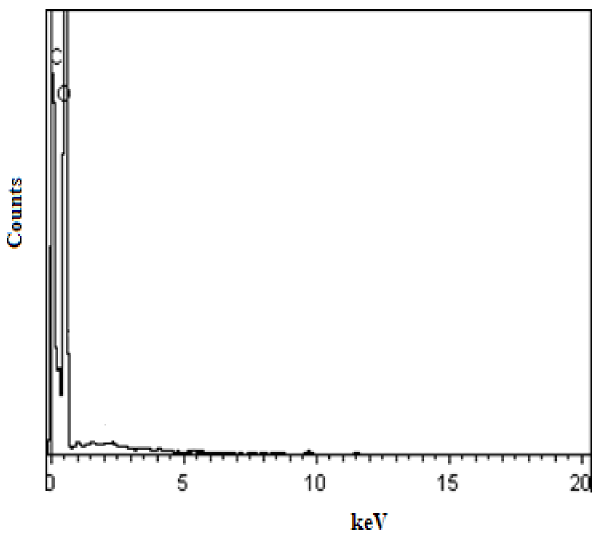

Fig.5: EDAX spectrum of lithium formate crystal

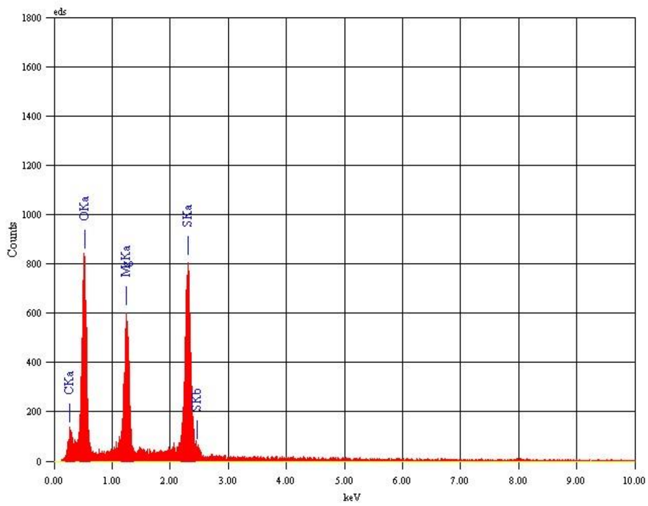

Fig.6: EDAX spectrum of magnesium sulfate doped lithium formate crystal

IV. CONCLUSIONS

Solution growth method was adopted to grow the undoped and magnesium sulfate doped lithium formate crystals. Solubility of lithium formate crystals is observed to be increasing when magnesium sulfate was added as dopant. The crystal structure of lithium formate monohydrate crystal is not changed on addition of magnesium sulfate as the

dopant. SHG efficiency and hardness of the sample are found to be enhanced when lithium formate crystals are doped with magnesium sulfate. The LDT values of undoped and magnesium sulfate doped lithium formate crystals were found to be 1.46 GW/cm^2 and 1.63 GW/cm^2 respectively. The elements of the samples have been identified by EDAX analysis. Dielectric parameters have been enhanced when lithium formate crystals were doped with magnesium sulfate.

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